# Self-assembly of an Anion Binding Cryptand for the Selective Encapsulation, Sequestration and Precipitation of Phosphate from Aqueous Systems.

Craig R. Rice,* Christopher Slater, Robert A. Faulkner and Robert L. Allan.

**Abstract:** The self-assembled trimetallic species $[L_2Cu_3]^{6+}$ contains a cavity that acts as a host to many different anions and using X-ray crystallography, ESI-MS and UV-Vis we show that these anions are encapsulated both in the solid-state and aqueous systems. Upon encapsulation the anions $Br^-$, $I^-$, $CO_3^{2-}$, $SiF_6^{2-}$, $IO_6^{3-}$, $VO_4^{3-}$, $WO_4^{2-}$, $CrO_4^{2-}$, $SO_4^{2-}$, $AsO_4^{3-}$ and $PO_4^{3-}$ are all precipitated from aqueous solution and can be removed by filtration. Furthermore, the cavity can be tuned to be selective to either phosphate or sulfate anions by variation of the $p$H. Phosphate anions can be removed from water, even in the presence of other common anions, reducing the concentration from 1000 to < 0.1 ppm and recovering ~99% of the phosphate anion.

Anions are essential to all living systems and permeate the environment that supports them. For example, the phosphate anion is both a vitally important fertilizer[1] and a pollutant as it is a primary cause of eutrophication.[2] Despite their obvious environmental and agricultural significance, the ability of the chemist to detect and sequester anions in aqueous (or other) media has significantly lagged behind their cationic counterparts. In order to remediate this discrepancy in knowledge, much effort has been focused upon the synthesis of receptors capable of binding anions.[3] Consequently, there are an increasing number of examples of molecules containing hydrogen-bond donor atoms capable of binding anions. However, many receptors are difficult to prepare, require multi-step syntheses and are often limited to non-aqueous environments and there are only a limited number of reported examples of receptors that recognize anions in water.[4] One method to circumvent complex synthetic procedures is to generate anion receptors from self-assembly, where the receptor is not synthesized in the conventional sense but assembled in solution, generating a complex architecture from smaller pre-programmed chemical fragments.[5,6] However, despite the production of complex anion-binding cavities from this self-assembly process, to date the vast majority of these species are limited to binding anions of low charge density (e.g. $PF_6^-$, $BF_4^-$, $ClO_4^-$) in non-competitive organic solvents. Despite all the on-going research into anion receptors the formation of species that can selectivity bind and sequester anions from aqueous media still remains a significant challenge which for agricultural and environment reasons is becoming increasingly urgent.

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This work demonstrates a self-assembled cationic trinuclear species (e.g. $[L_2Cu_3]^{6+}$) which contains a cavity within the core of the molecule. We demonstrate both in aqueous and solid state media a variety of different anions that can be encapsulated within this core, allowing selective and efficient removal from aqueous systems.
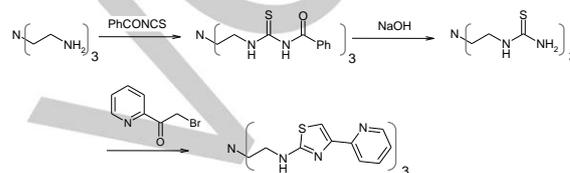


**Scheme 1.** Synthesis of ligand L.

Reaction of ligand L with 1.5 equivalents of $Cu(BF_4)_2$ in nitromethane gave a light blue coloured solution. This produces an ion at $m/z$ 1877 in the ESI-MS corresponding to $\{[L_2Cu_3](BF_4)_5\}^+$ indicating the formation of a trinuclear assembly. Blue crystals of this material were deposited upon slow diffusion of diisopropyl ether and analysis by X-ray diffraction confirmed the formation of $[L_2Cu_3]^{6+}$. In the solid state each of the three bidentate pyridyl-thiazole domains on the ligand strand coordinates a different copper metal ion and in turn each metal ion is coordinated to two separate ligands resulting in coordination by a total of four N-donor atoms, two from each ligand (Fig 1). In the centre of the self-assembled species is a cavity which in this case contains an encapsulated $BF_4^-$ anion. This single anion is held within this cavity by a total of nine interactions comprising of three Cu····F coordination bonds and six -NH····F hydrogen bonding interactions. In the complex, each of the three copper ions coordinate one of the fluorine atoms and this interaction is supplemented by a -NH···F hydrogen bond from the amine units on the ligand chain. The uncoordinated fluorine atom points upward from the "Cu₃" core and interacts with the remaining three –NH units.
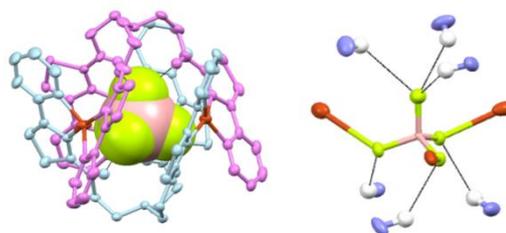


**Figure 1**. X-ray structure of $[L_2Cu_3(BF_4)]^{5+}$ showing the coordination and hydrogen bonding of the anion. Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms and anions are omitted for clarity.

Other anions can be encapsulated within the cavity formed by the $[L_2Cu_3]^{6+}$ cation. Reaction of two equivalents of ligand L, three equivalents of $Cu(BF_4)_2$ and one equivalent of $Et_4NBr$ in $MeNO_2$ gave, after slow diffusion of diisopropyl ether, a homogeneous mass of large blue crystals. Analysis by single-crystal X-ray diffraction showed the expected $[L_2Cu_3]^{6+}$ fragment

but now containing a bromide anion within the core (Fig 2). The size of the spherical bromide anion is such that it sits to one side of the cavity, coordinating two of the three Cu(II) ions and forming hydrogen bonds to two pairs of -NH donor units above and below the trimetallic plane.
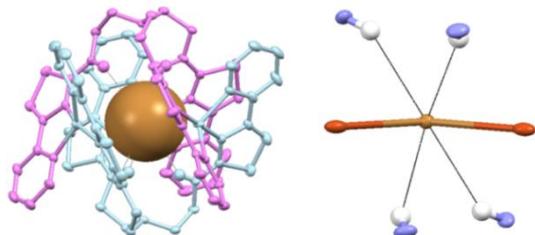


**Figure 2**. X-ray structure of $[L_2Cu_3(Br)]^{5+}$ showing the coordination and hydrogen bonding of the anion. Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms and anions are omitted for clarity.

The complex not only acts as a host to spherical and tetrahedral anions, since reaction of $[L_2Cu_3]^{6+}$ with $Na_2SiF_6$ demonstrates that the octahedral divalent anion $SiF_6^{2-}$ is also encapsulated within the cavity. Here, each of the Cu(II) ions coordinate two fluoride anions and each fluoride forms a hydrogen bond to each -NH donor unit (Fig 3).
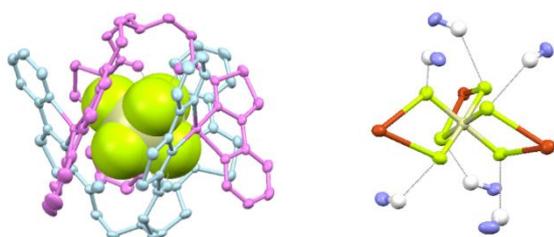


**Figure 3**. X-ray structure of structure of $[L_2Cu_3(SiF_6)]^{4+}$ showing the coordination and hydrogen bonding of the anion. Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms and anions are omitted for clarity.

Interestingly the $[L_2Cu_3]^{6+}$ capsule complex can also be formed in aqueous media and acts a host to different anions giving a variety of colours (Fig 4a).



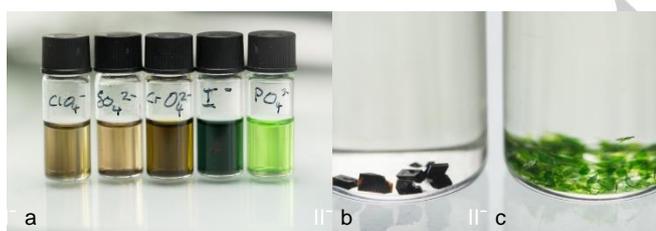**Figure 4**. a) Aqueous solutions of $[L_2Cu_3]^{6+}$ with a variety of anions. A solution of $[L_2Cu_3]^{6+}$ which has been reacted with (b) $HSO_4^-$ and (c) $H_2PO_4^-$ and deposits brown and green crystals respectively.

For example, reaction of two equivalents of ligand L, three equivalents of $Cu(ClO_4)_2$ in a solution of MeCN and $H_2O$ (in a ratio 1:4) produced a pale tan-coloured solution which turns lime green upon reaction with one equivalent of $Bu_4NH_2PO_4$. This solution was then allowed to evaporate (removing the organic solvent) giving a colourless solution and a homogeneous lime green crystalline precipitate (Fig 4b and c).
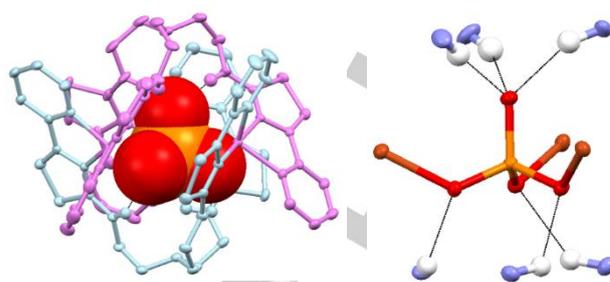


**Figure 5**. X-ray structure of $[L_2Cu_3(PO_4)]^{3+}$ showing the coordination and hydrogen bonding of the anion. Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms and anions are omitted for clarity.

Examination by X-ray crystallography showed the formation of $[L_2Cu_3]^{6+}$ and within it an encapsulated phosphate anion. In an analogous fashion to the tetrahedral tetrafluoroborate anion the three $Cu^{2+}$ atoms coordinate the anion (in this case three of the oxygen atoms) and this is supplemented by three -NH···O hydrogen bonding interactions (Fig 5). The remaining uncoordinated oxygen atom forms hydrogen bonds to three -NH donor units within the "upper rim" of the cavity. It is worth noting that even though dihydrogen phosphate is added to the assembly this undergoes deprotonation giving $PO_4^{3-}$ which can be demonstrated by the presence of three perchlorate counter ions in the solid state and due to the trivalent anion three perchlorate anions are released into solution.

Encapsulation has been carried out with a range of tetrahedral counter ions *viz.* $VO_4^{3-}$, $WO_4^{2-}$, $CrO_4^{2-}$, $SO_4^{2-}$ and $AsO_4^{3-}$ by reaction of $[L_2Cu_3]^{6+}$ with one equivalent of anion in aqueous media. In all cases an isostructural species with inclusion of the anion in the core is observed and hydrogen bonding from the -NH units and coordination to the Cu(II) ions is observed in an analogous fashion to $[L_2Cu_3(PO_4)]^{3+}$ (Fig 6a - e).

The only tetrahedral anion that behaves anomalously is $IO_4^-$, which undergoes hydrolysis in the presence of $[L_2Cu_3]^{6+}$ forming the tetranuclear species $[L_2Cu_4(IO_6)]^{4+}$ (Fig 6f). In this assembly all four Cu(II) atoms coordinate two oxygen atoms, supplemented by six -NH···O interactions. Two of the Cu(II) ions are coordinated by two pyridyl-thiazole bidentate units and two anion oxygen atoms. The remaining two Cu(II) ions are coordinated by one bidentate ligand domain, two anion oxygen atoms and a molecule of water. The expansion of the trinuclear species arises as a consequence of the $IO_6^{3-}$ anion inducing a self-assembly change (*i.e.* inclusion of an extra Cu(II) ion to accommodate the larger anion *c.f.* $SiF_6^{2-}$).

In the case of $VO_4^{3-}$, $WO_4^{2-}$, $CrO_4^{2-}$, $SO_4^{2-}$ and $AsO_4^{3-}$ the same solubility profile is observed as the phosphate anion and upon addition of the anion to a solution of $[L_2Cu_3]^{6+}$ in water, containing a small amount of organic solvent, crystals of $[L_2Cu_3(EO_4)]^{n+}$ are deposited within a few minutes to days depending upon the concentration and the anion used (see Fig 4c).

Binding of halides has also been explored in aqueous solution with crystallisation of $[L_2Cu_3I]^{5+}$ occurring by reaction of $Et_4NI$ with $[L_2Cu_3]^{6+}$ in MeCN and water (ratio 1:4). This structure is similar to $[L_2Cu_3Br]^{5+}$ described earlier but the iodide, due to its larger size, sits equidistant to the three $Cu^{2+}$ ions but still forming four hydrogen bonds to two pairs of -NH donor units (Fig 7a).
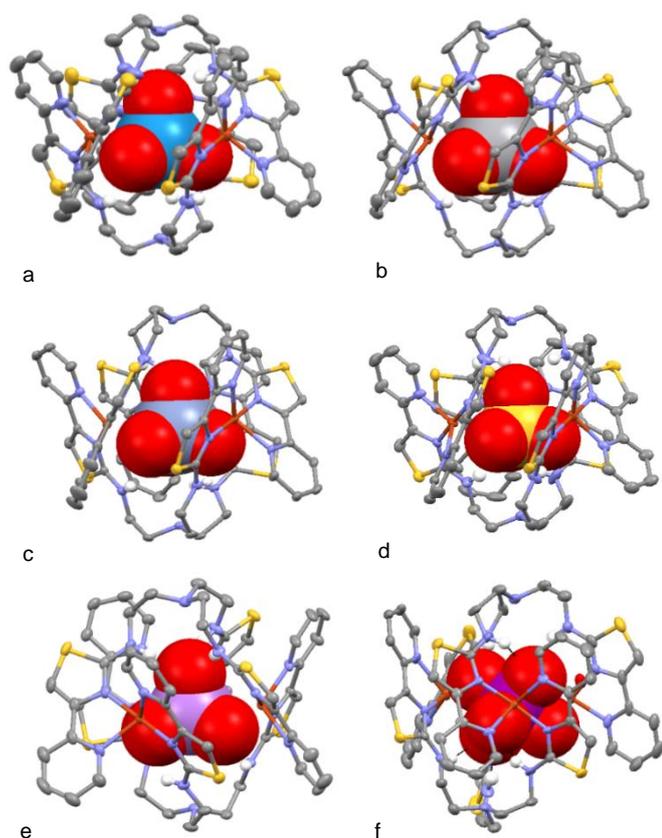
**Figure 6.** X-ray structure of (a) $[L_2Cu_3(VO_4)]^{3+}$, (b) $[L_2Cu_3(WO_4)]^{4+}$, (c) $[L_2Cu_3(CrO_4)]^{4+}$, (d) $[L_2Cu_3(SO_4)]^{4+}$, (e) $[L_2Cu_3(AsO_4)]^{3+}$ and f) $[L_2Cu_4(IO_6)]^{4+}$. Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms and anions are omitted for clarity.

Interestingly, addition of $ReO_4^-$ to $[L_2Cu_3](trif)_6$ does deposit dark blue crystals after 48 hrs, but analysis by X-ray crystallography shows that the perrhenate is not included within the $[L_2Cu_3]^{6+}$ molecule but instead acts as a simple counter ion. However, inside the cavity is a $CO_3^{2-}$ anion which coordinates two of the Cu(II) ions and forms hydrogen bonds to the six -NH donors (Fig 7b). A virtually identical species is observed when a sample of $[L_2Cu_3](trif)_6$ is allowed to stand for several days. It therefore seems likely that the included anion is due to the presence of $CO_2$ within the aqueous solution which is hydrolysed and subsequently encapsulated within the host. UV-Vis studies show that the reaction with $CO_2$ is complete within 1 hr and the encapsulated carbonate can be displaced with dihydrogen phosphate giving $[L_2Cu_3(PO_4)]^{3+}$. This type of behaviour isn't unprecedented and has been observed in other supramolecular assemblies.[7]

Reaction of Cu(II) (with either $ClO_4^-$, $BF_4^-$ or triflate counter ions) with 1.5 equivalents of L in $H_2O$/MeCN (4:1) gives a pale tan coloured solution and a UV-Vis spectrum of this shows the main absorption at 810 nm. Reaction of this with a variety of anions shows a change in the UV-Vis spectrum; with some (such as iodide) resulting in a dramatic increase in absorption with a concomitant change in the solution colour (see Fig 4a). On the other hand, a shift to higher energy was observed for $H_2PO_4^-$ (740 nm). The changes in the absorption spectrum arise as each anion coordinates the Cu(II) metal ion and modulates the

response of the chromogenic ion. Conversely, no absorbance change was observed with the addition of the nitrate anion, indicating that the cavity does not act as a host in this instance.
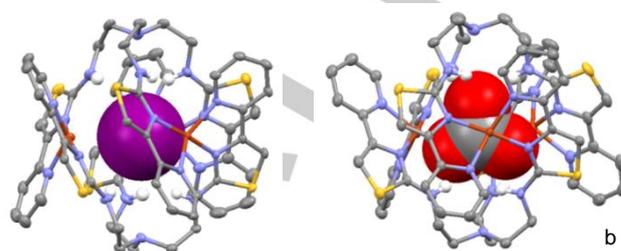


**Figure 7**. a) X-ray structure of a) $[L_2Cu_3(I)]^{5+}$ and b) $[L_2Cu_3(CO_3)]^{4+}$. Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms and anions are omitted for clarity.

Analysis of the complexes by ESI-MS also demonstrated that anions were encapsulated in the gas phase. For example, the ESI-MS of the sulfate sample shows an ion at $m/z$ 1839 corresponding to $\{[L_2Cu_3(SO_4)](BF_4)_3]\}^+$ and the phosphate derivative shows an ion at $m/z$ 1736 corresponding to $\{[L_2Cu_3(PO_4)](ClO_4)_2\}^+$. This behaviour is also observed for the $SiF_6^{2-}$, $VO_4^{3-}$ and $WO_4^{2-}$ analogues. Analysis of the crystals of the $CO_3^{3-}$ derivative shows a remarkably simple spectrum with an ion at $m/z$ 1952 corresponding to $\{[L_2Cu_3(CO_3)](trif)_3\}^+$ thus confirming the presence of carbonate within the central core. The halide examples were slightly more complex with the iodide complex containing ions at $m/z$ 1967 and 1940 corresponding to $\{[L_2Cu_3(I)](ClO_4)_4\}^+$ and $\{[L_2Cu_3](ClO_4)_5\}^+$ respectively, thus demonstrating that in the gas phase the halide can be lost. ESI-MS analysis of both $IO_6^{3-}$ and $CrO_4^{2-}$ are difficult to assign and this is attributed to the reactive nature of these anions which interferes with the mass spectrometry process.

In a series of competitive experiments, the cavity containing complex was reacted with one equivalent of $Cl^-$, $Br^-$, $I^-$, $NO_3^-$ and $SO_4^{2-}$ and in each case their UV-Vis spectrum was recorded. To this was then added one equivalent of $Bu_4NH_2PO_4$ and in virtually all cases, the resultant spectrum was identical to that of $[L_2Cu_3](PO_4)]^{3+}$ indicating that the initially added anion was displaced by the phosphate anion. This could be observed with the naked eye as in virtually all cases the characteristic lime-green colour was generated upon addition of the dihydrogen phosphate anion. However, upon reaction of $[L_2Cu_3]^{6+}$ with $HSO_4^-$ and then $H_2PO_4^-$, no change is observed in the UV-Vis, indicating that the dihydrogen phosphate did not displace the anion and $[L_2Cu_3(SO_4)]^{4+}$ remained intact. However, addition of $SO_4^{2-}$ and then $HPO_4^{2-}$ resulted in the characteristic lime-green colour and the UV-Vis showed the formation of $[L_2Cu_3(PO_4)]^{3+}$ indicating that a higher $p$H (where $SO_4^{2-}$ and $HPO_4^{2-}$ would predominate) the cavity is selective to phosphate (see ESI).

The selectivity of the cavity can be rationalised in terms of charge and shape of the potential anion host. Monoanionic trigonal planar and tetrahedral anions are either displaced easily (*c.f.* $BF_4^-$) or are not encapsulated ($NO_3^-$) whereas spherical anions can act as hosts (c.f. $Br^-$ and $I^-$). Dianionic trigonal planar anions ($CO_3^{2-}$) are included within the core (*c.f.* $NO_3^-$) and all the di- and trivalent tetrahedral anions are readily encapsulated. The selectivity is related to the charge and shape of the anion with $PO_4^{3-}$ displacing all the lower charged species. However, for

both phosphate and sulfate anions which are tetrahedral and polyprotic, the cavity is selective for $HSO_4^-$ over $H_2PO_4^-$ but then reversed for $SO_4^{2-}$ and $HPO_4^{2-}$. This can be rationalised by the acidity of the mono-anion which is significantly more acidic for $HSO_4^-$ ($pK_a = 1.81$) than $H_2PO_4^-$ ($pK_a = 7.21$) because it is easier to deprotonate $HSO_4^-$, this will occupy the cavity in preference to dihydrogen phosphate.

The use of this complex isn't limited to triflate, perchlorate and tetrafluoroborate counter anions (*i.e.* $[L_2Cu_3](PO_4)]X_3$ where X = $CF_3SO_3^-$, $ClO_4^-$ and $BF_4^-$) since we have isolated $[L_2Cu_3](PO_4)](NO_3)_3$ from which the "$[L_2Cu_3]^{6+}$" unit was initially prepared from $Cu(NO_3)_2$ (see ESI). Furthermore, $Cu(NO_3)_2$, $Cu(OAc)_2$ and $CuCl_2$ react with the ligand and give the same characteristic lime-green colour upon reaction with dihydrogen phosphate and give the expected absorption at 740 nm. However to date, we have been unable to characterise them in the solid state.

To investigate how much of the phosphate anion was consumed the amount of phosphate anion present in solution was measured by ion chromatography. In an experiment a 1000 ppm solution of hydrogen phosphate was reacted with a slight excess of $[L_2Cu_3](ClO_4)_6$ and the solution was allowed to stand for 48 hrs during which time a lime-green crystalline precipitate had formed. Analysis of the remaining colourless solution showed that the concentration of phosphate had reduced to < 0.1 ppm. In a similar experiment the green crystalline mass was isolated and dried and showed that recovery of the material was ~ 99% of $[L_2Cu_3(PO_4)](ClO_4)_3$ indicating a nearly quantitative recovery/removal of the phosphate anion. In a competitive experiment, a solution containing 50 ppm of each of $Cl^-$, $NO_3^-$, $SO_4^{2-}$ and $HPO_4^{2-}$ anions was reacted with one equivalent of $[L_2Cu_3](trif)_6$ and the solution allowed to stand for a week during which time a green crystalline precipitate formed. The solution was then analysed by ion chromatography revealing the presence of 47 ppm of chloride, 46 ppm nitrate, 41 ppm sulfate and 10 ppm phosphate. This demonstrates that the complex is highly selective to phosphate, in the presence of a series of common anions in aqueous media, hence removing ~80% of this anion.

We have shown that the ligand L forms a trinuclear species with Cu(II) containing a central cavity which can act as a host to a variety of anions. Upon encapsulation the host can form a total of six $-NH\cdots A^{n-}$ interactions as well as three $Cu\cdots A^{n-}$ coordination bonds. The host is selective to both size and shape and is particularly selective to the highly charged tetrahedral phosphate anion. This is demonstrated in solution where in a competitive medium (i.e. water) the host binds anions in a stochiometric manner and can remove anions from water at very low concentration in almost quantitative yield. It is also noteworthy that the complex is retained in the presence of coordinating anions such as phosphate and sulfate, as anions such as these have been shown to both change[6,8] and disassemble[9] supramolecular assemblies of this nature. Due to its selectivity and efficiency of binding phosphate this $[L_2Cu_3]^{6+}$ complex is a promising candidate for the removal and remediation of phosphate anions in aquatic systems and it, and other complexes based on this type of architecture, will be of definite interest for further study.

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## COMMUNICATION

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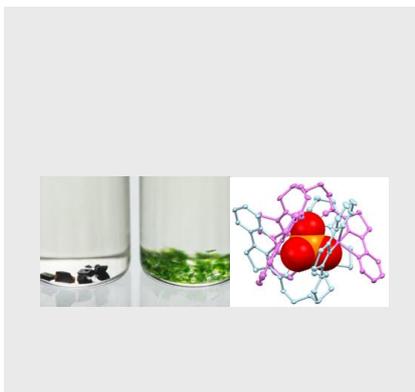
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